



PATENT SPECIFICATION

NO DRAWINGS

936.057

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Date of Application and filing Complete Specification: Nov. 20, 1961.
No. 41412/61.

Complete Specification Published: Sept. 4, 1963.

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Index at acceptance:—Class 2(6), P7A, P7C(11:12B:12X:13B:13C:18:20A:20B:20D1), P7D(1A:1B:1X:2A1), P7(K7:T2A), P8A, P8C(11:12B:12X:13B:13C:18:20A:20B:20D1), P8D3A, P10A, P10C(11:12B:12X:13B:13C:18:20A:20B:20D1), P10D1A.

International Classification:—C08f.

COMPLETE SPECIFICATION

Polymer Compositions and their preparation

We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a company organised under the laws of The Netherlands, of 30, Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to polymer compositions comprising thermoplastic synthetic organic polymers for example polyolefins, polyvinyl-aromatic compounds, polyvinylchloride, acrylonitrile polymers and copolymers. Although not limited thereto, the present invention is particularly applicable to polymer compositions comprising hydrocarbon polymers particularly polyolefins and olefin copolymers (the term polymer is therefore used herein to include copolymers).

For some applications of thermoplastic synthetic organic polymers, e.g. polyolefins, polystyrene and polyvinyl chloride, it is desirable to increase the rigidity of the polymer by the incorporation of filler materials therein. Such fillers should be sufficiently compatible with the polymer to permit the formation of a homogeneous dispersion and it is desirable that the fillers should also be relatively cheap materials. A particular application of filled thermoplastic organic polymers is the production of pipe. Frequently pipes of water supply and disposal have to be buried in the ground and there is also an increasing use of thermoplastic pipes for land drainage purposes. Since many soils are slightly acidic it is necessary in such case to use a filler which is substantially unaffected by acid conditions in the ground in which the pipe is buried and this requirement precludes the use of for example metal oxide, hydroxide and carbonate filler materials which are not acid resistant.

The applicants have now found that certain

finely-divided inorganic sulphates which have a proportion of organic material associated therewith are particularly suitable fillers for synthetic organic thermoplastic polymers.

According to the present invention a polymer composition comprises a blend of a synthetic organic thermoplastic polymer and a finely-divided filler having an average particle size between 5 microns and 100 microns, said filler comprising a sulphate of a metal of Group 2 of the Periodic Classification having therewith in physical association (as hereinafter specified) a higher fatty acid (as hereinafter specified) or a salt or an ester thereof.

Advantageously said polymer composition contains at least 20% (by weight of said polymer) of said filler, and said filler preferably has a particle size below 90 microns, more preferably below 65 microns.

Although the present invention can be applied to synthetic organic thermoplastic polymers in general it is particularly useful in the case of polyolefins and in particular low-pressure polyolefins that is to say polyolefins which have an essentially linear molecular structure and relatively high densities as compared with the branched chain polyolefins, the densities being, in the case of linear polyethylenes, above about 0.93. Such low-pressure polyolefins include the so-called Ziegler polyolefins, e.g. polyethylene, obtained by polymerising olefinic compounds i.e. hydrocarbon compounds containing a carbon/carbon double bond (in particular alpha-olefins) at pressures below 500 atmospheres and usually below 50 atmospheres with the aid of a Ziegler catalyst. Ziegler catalysts and the Ziegler process for preparing polyethylene are described for example in U.K. Patent Specifications Nos. 799,392; 799,823; and 801,031. Ziegler catalysts can be formed by mixing at least two catalyst-forming components as indicated for example in the Specification of our U.K.

Patent Specification No. 867,566, and the Ziegler process can be used for polymerising e.g. ethylene, propylene or butylene or a mixture containing two or more such olefins.

- 5 High density linear polyethylene has the advantage compared with the low density branched chain polyethylene produced by high-pressure polymerisation, of having a higher softening point and also other useful properties which make it eminently suitable for fabrication into shaped articles by fabrication techniques known per se, e.g. by moulding, blowing, extruding and pressing, which articles can be used in a large number of applications.
- 10 Moreover the physical properties of such high density linear polyethylene can be modified by blending with elastomers or with other polyolefins e.g. polypropylene.

- In an article by Bostwick et al in "Industrial and Engineering Chemistry" 42, pages 848—9 (1950) it is suggested that the incorporation of simple inorganic fillers, namely silica; clay; calcium carbonate; carbon black; magnesium carbonate and calcium sulphate, in polyethylene can increase the stiffness of the polyethylene but the experimental results obtained by Bostwick et al and quoted in this article show that the filled polyethylene is less resistant to cracking or breaking when bent sharply as compared with unfilled polyethylene. It was therefore concluded in this article that the incorporation of inorganic fillers in polyethylene has disadvantages as well as advantages. Surprisingly it has now been found by the Applicants that the stress-cracking resistance of high density linear polyethylene, particularly Ziegler polyethylene, can be improved in some cases at least by incorporating therein the above-defined inorganic sulphate fillers. The Applicants' investigations have in fact indicated that in many instances the incorporation of such fillers in high density linear polyethylene can not only increase the stress-cracking resistance of the polyethylene but can at the same time improve its ultimate elongation properties.

- According therefore to a particular aspect of the present invention a polymer composition comprises a blend of a polyolefin having a substantially linear molecular structure and a finely-divided filler having a particle size between 5 microns and 100 microns, said filler comprising a Group 2 metal sulphate having therewith in physical association (as specified hereinafter) a higher fatty acid (as specified hereinafter) or a salt or an ester thereof. Preferably, and particularly in the case of a low-pressure polyethylene compositions, said filler has a particle size below 90 microns, more preferably below 65 microns, and advantageously said polyolefin composition contains at least 20% of said filler by weight of said polyolefin. Up to 100% by weight of filler can be used in some circumstances.

- 65 For many applications of the polymer com-

positions of the present invention the presence of a minor amount (based on the polymer) of an elastomer may be highly desirable from the point of view of increasing the impact strength of the polymer and it has been found that polymer compositions as defined above which also have between 5 and 20%, e.g. of the order of 10—15% in the case of polyethylene compositions, of an elastomer blended therewith are particularly useful in this respect. Suitable elastomers include natural and also synthetic rubber e.g. butyl rubber, GRS rubber, polyisobutylene, polybutadiene, polyisoprene and nitrile rubber.

The sulphate fillers which can be used in carrying out the present invention are particulate Group 2 metal sulphates which are "activated" by, that is to say are in physical association with, a minor proportion by weight of an organic material which can be a higher fatty acid or mixture thereof (the term "higher" meaning a fatty acid having at least six carbon atoms in the molecule), and/or a salt or salts thereof or an ester or esters thereof. Preferably the organic material comprises a higher fatty acid(s) or salt(s) thereof and in particular a salt or salts which is/are preferably a Group 2 metal salt or salts, conveniently of the same Group 2 metal as the sulphate. The sulphate filler particles can be thinly coated with the organic material and in such case the activated sulphate filler can be produced by mixing, e.g. milling, the sulphate with the organic material; if desired the sulphate can be reduced to the required particle size at the same time. Preferably, however, the activated sulphate filler comprises Group 2 metal sulphate particles in association with a fatty acid(s) salt(s) of the same Group 2 metal and in such case the filler can be produced either by a coprecipitation technique from a solution containing a soluble Group 2 metal salt and a fatty acid salt or salts or by a precipitation technique in which a Group 2 fatty acid salt or salts is/are precipitated from a solution of a soluble salt or salts of the fatty acid or acids in which solution a particulate Group 2 metal sulphate is slurried. The Group 2 metal sulphate is advantageously calcium or barium sulphate, although the sulphates of other Group 2 metals and also mixtures of sulphates can also be used. The organic material associated with such sulphates is preferably a Group 2 metal stearate, e.g. calcium or barium stearate in the case of calcium or barium sulphate respectively.

When preparing the sulphate fillers for use in carrying out the present invention by the coprecipitation technique previously referred to a Group 2 metal sulphate is preferably coprecipitated with a Group 2 metal salt of a higher fatty acid by mixing an aqueous solution of a water-soluble Group 2 metal salt, e.g. a chloride, with an aqueous solution of an alkali metal or ammonium sulphate and an alkali metal or ammonium salt of a higher

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fatty acid e.g. stearic acid; followed by removal of the solid material, washing, drying and finally comminuting to the required particle size. The amount of fatty acid salt in the aqueous solution relative to the amount of alkali metal or ammonium sulphate should in general be about equal to the desired ratio of Group 2 metal fatty acid salt to Group 2 metal sulphate in the required filler. For example when preparing a filler consisting of calcium sulphate having 4% by weight of calcium stearate associated therewith the weight ratio of alkali metal (or ammonium) stearate to alkali metal (or ammonium) sulphate in the aqueous solution to which a solution of e.g. calcium chloride is added gradually with stirring to coprecipitate calcium sulphate and calcium stearate should be of the order of 3:100 to 5:100. Preferably the amount of Group 2 metal fatty acid salt associated with a Group 2 metal sulphate in the fillers of the present invention is of the order of 3 to 5% by weight e.g. between 2 and 6% by weight.

When preparing the sulphate filler by precipitation of a Group 2 metal salt of a fatty acid in the presence of a Group 2 metal sulphate, this is preferably effected by forming a slurry of the Group 2 metal sulphate in an aqueous solution of an alkali metal or ammonium salt of a higher fatty acid e.g. sodium stearate and adding thereto, with stirring at least a stoichiometric amount of a water-soluble Group 2 metal salt, e.g. calcium chloride, in the form of an aqueous solution, after which the solid material is removed, washed and dried.

Preferably preparation of the sulphate fillers for use in carrying out the present invention (either by the precipitation or coprecipitation technique) is carried out at about ambient temperature, the aqueous solutions and slurries being at temperatures of the order of 18 to 25°C. In general the sulphate fillers after precipitation (or co-precipitation) will require washing to remove water-soluble salt and then drying, after which comminution to the desired particle size will usually be necessary. For convenience the fatty acid salt will usually be a salt of the same Group 2 metal as is present in the sulphate e.g. calcium or barium stearate in association with calcium or barium sulphate respectively, though this is not essential and e.g. barium stearate can be associated with e.g. calcium sulphate if desired.

As previously indicated the particle size of the coated sulphate fillers should be below 100 microns and preferably below 90 microns (i.e. such that passing a 150 mesh B.S.S. sieve). Preferably, from the point of view of obtaining optimum stress cracking and ultimate elongation properties in polyolefin compositions in accordance with the present invention and in particular in those comprising Ziegler polyolefins especially polyethylene, the coated sulphate filler should have a particle size be-

tween 5 and 65 microns and advantageously as small as possible within this range. The amount of coated sulphate filler of defined particle size is advantageously between about 10 and 100% and preferably between 20 and 60% by weight of the polyolefin. It will be understood that the polymer compositions of the present invention can contain a small amount of sulphate filler lying outside the particle size defined herein and this will often be the case since in operations on a manufacturing scale it is usually not possible or at least not economically feasible to ensure that all particles of a particulate solid additive lie within a defined particle size. The essential requirement in respect of particle size is therefore that at least part (and usually at least 10% by weight of the polymer) of the polymer composition consists of sulphate filler of the defined particle size or considered in terms of the production of the polymer compositions of the present invention, from sulphate fillers of the defined particle size, the polymer e.g. the polyolefin (which may of course also contain other additives e.g. antioxidants) is blended with the required amount of coated sulphate filler, usually an amount such that at least 10% (by weight of the polymer) of the sulphate filler has a particle size as defined.

As previously indicated the sulphate filler of the polymer compositions of the present invention can be reduced to the required particle size during the preparation of the compositions, if desired; though preferably at the outset the fillers within the defined particle size range are used in preparing the polymer compositions.

The present invention is particularly applicable to polyolefins obtained by the Ziegler process and in particular polyethylene and polypropylene and copolymers thereof. For example compositions can be produced from Ziegler polyethylene formed for example by polymerising ethylene in the presence of a catalyst formed by mixing a Group 4A metal (e.g. titanium) tetrahalide or trihalide in particular a chloride with an organo-aluminium compound in particular an aluminium trialkyl, aluminium alkyl halide or aluminium alkyl alkoxide as for example a catalyst formed by mixing titanium tetrachloride or titanium trichloride with aluminium diethyl chloride.

The present invention also includes a process for preparing a polymer composition, which comprises blending a synthetic organic thermoplastic polymer, e.g. a polyolefin in particular a polyolefin having a substantially linear molecular structure, with a finely-divided filler having a particle size between 5 microns and 100 microns, said filler comprising a Group 2 metal sulphate having therewith in physical association (as specified herein) a higher fatty acid (as specified herein) or a salt or an ester thereof.

The polymer compositions of the present in-

vention can be formed by blending one or more synthetic organic thermoplastic polymers e.g. polyolefins with a sulphate filler or fillers by conventional blending technique such as by mechanically working a mixture of the polymer(s), e.g. polyolefin(s), and sulphate filler(s), at an elevated temperature in the region of the softening or melting point of the polymer(s) e.g. in the case of polyethylene or polypropylene by milling or extruding at 140 to 180°C, to produce a substantially homogeneous composition, and if desired a masterbatch can be prepared from polymer and filler and thereafter mixed with a further amount of polymer. Such blending techniques are well known per se in the polymer art and do not require detailed description herein. It will be understood that compositions based on polyolefins in accordance with the present invention will usually also include stabilisers for the polyolefin e.g. to prevent (or to counteract the effect of) oxidation or degradation of the polyolefin as a result of exposure to heat during processing, i.e. during preparation of the blend and its subsequent fabrication into shaped articles, and as the result of the effect of ultraviolet radiation during subsequent use of the articles. Any known or suitable stabilisers used either singly or in combination in appropriate amounts can be present in the polyolefin-containing compositions of the present invention which can also include other additives e.g. pigments and other colouring matter, anti-static additives, mould release agents, elastomeric materials and other agents added for special purposes. In the case of blends formed from Ziegler polyethylene stabilisers of the organic phosphite, phenolic, inorganic or organic sulphide; amine or thiophosphite type are frequently used. It is also possible to include peroxide cross-linking agents associated with the sulphate fillers, e.g. dicumyl peroxide or ditertiary-butyl peroxide for the purpose described in e.g. U.K. Patent Specification No. 789,116.

The present invention may be illustrated by the following examples:—

EXAMPLE I.

A Ziegler polyethylene having a melt index (as determined by the standard cup method—British Standard 1972/52) of 0.23 was used for preparing blends in accordance with the present invention. The polyethylene contained 0.02 parts by weight of "Santonox" per hundred parts by weight of the polyethylene as an anti-oxidant stabiliser. The word "Santonox" is a trade designation for 4,4'-thiobis(3-methyl-6-tert.-butyl phenol). Blends were prepared by milling the polyethylene with 25 parts by weight per 100 parts by weight of the polyethylene of various stearate-containing sulphate fillers prepared by the coprecipitation technique in the following manner:—

An aqueous solution containing sodium sulphate and sodium stearate was prepared and aqueous calcium (or barium) chloride added to coprecipitate calcium (or barium) sulphate in admixture with calcium (or barium) stearate, the ratio of sulphate to stearate in the coprecipitate being equal to the ratio of sodium sulphate to sodium stearate in the starting solution. The precipitate was washed several times with water and then air-dried at 110°C after which it was crushed to a particle size which passed a 240 mesh B.S.S. sieve i.e. the average particle size was less than 64 microns. Three sulphate fillers were prepared in this way, namely BaSO₄ containing 2% and 4% by weight of barium stearate and CaSO₄ containing 4% by weight of calcium stearate.

The various blends were tested, in the form of small moulded test pieces, for stress-cracking resistance by bending and determining the period before cracking occurred in the test piece. In addition the ultimate elongation was determined on a moulded test piece of each blend. The results obtained are indicated in the following Table I, in which the abbreviation p.h.r. means parts by weight per hundred parts by weight of polyethylene:

TABLE I

Filler	Ultimate Elongation %	Stress, Cracking (Hours)
a) None	540	5 to 10
BaSO ₄ alone	Broke on yield	23½
CaSO ₄ alone	Broke on yield	305
b) BaSO ₄ plus:—		
1.5% stearate	450	23
2.0% stearate	840	289
4% stearate	870	480
c) CaSO ₄ plus		
4% stearate	790	377

EXAMPLE II.

5 This example illustrated the improvement in ultimate elongation properties which may be obtained by addition of relatively small amounts of coated sulphate fillers in accordance with the present invention. A calcium sul-

phate containing 4% calcium stearate was incorporated in the Ziegler polyethylene referred to in Example I. The coated calcium sulphate had an average particle size of less than 64 microns. The results obtained are indicated in the following Table II.

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TABLE II

Filler	Ultimate Elongation %
(a) None	540
(b) CaSO ₄ plus 4% calcium stearate	
0.2 phr of filler	820
2.0 phr of filler	840
5.0 phr of filler	890

15 In general calcium sulphate containing 1 to 6% by weight of calcium stearate, preferably 3 to 5% by weight thereof, is a preferred additive for forming compositions from Ziegler polyethylene in accordance with the present invention, though barium sulphate containing barium stearate is also suitable. The organic component of the sulphate is preferably a Group 2 metal stearate and about 4% (by weight of the sulphate) of such a stearate is an advantageous proportion, although other amounts such as 3 to 5% by weight of stearate can be used.

EXAMPLE III.

Blends were made from the polyethylene referred to in Example I and 25 p.h.r. of various fractions (obtained by sieving) of (a) CaSO₄ plus 4% calcium stearate and (b) BaSO₄ plus 4% barium stearate, each blend containing 0.02 p.h.r. of "Santonox", and the physical properties of the blends were determined as indicated in the previous example. The results obtained are indicated in the following Table III:—

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TABLE III

Average Particle Size of Filler	Ultimate Elongation %	Stress Cracking (Hours)
(a) CaSO_4 plus 4% calcium stearate		
90 microns	880	311
below 80 microns	860	311
(b) BaSO_4 plus 4% barium stearate		
70 microns	700	648
below 64 microns	600	600

EXAMPLE IV.

This example illustrates the use of a sulphate filler prepared by the precipitation technique. A slurry of powdered calcium sulphate in 2% (by weight) aqueous sodium stearate was mixed with a stoichiometric excess of aqueous calcium chloride with constant stirring, the amount of calcium sulphate in the slurry being such that the amount of calcium stearate formed was 4% by weight of the calcium sul-

phate. The resulting solid material comprising particulate calcium sulphate in physical association with calcium stearate and having an average particle size below 80 microns was blended with Ziegler polyethylene containing 0.02 p.h.r. of "Santnox"; the amount of sulphate filler in the resulting polymer composition being 25 p.h.r. The results of physical tests on the polyethylene composition are shown in the following Table IV:—

TABLE IV

Additive	Yield Stress (Psi.)	Yield Elong'n (%)	Ult. Stress (Psi.)	Ult. Elong'n (%)	Stress Cracking (Hours)
None	3330	15	1970	540	5—10
25 phr calcium sulphate	3340	15	1810	670	648

WHAT WE CLAIM IS:—

1. A polymer composition which comprises a blend of a synthetic organic thermoplastic polymer and a finely-divided filler having an average particle size between 5 microns and 100 microns, said filler comprising a sulphate of a metal Group 2 of the Periodic Classification having therewith in physical association (as herein specified) a higher fatty acid (as herein specified) or a salt or an ester thereof.
2. A composition as claimed in claim 1, which contains at least 20% by weight (of said polymer) of said filler.
3. A composition as claimed in claim 1 or claim 2, wherein said polymer is a polyolefin.
4. A composition as claimed in claim 3,

wherein said polymer is a polyolefin having a substantially linear molecular structure.

5. A composition as claimed in any one of the preceding claims, wherein said sulphate is physically associated with a Group 2 metal salt of a higher fatty acid.

6. A composition as claimed in claim 5, wherein said sulphate is a coprecipitate prepared by mixing in aqueous solution an alkali metal or ammonium sulphate, an alkali metal or ammonium salt of a higher fatty acid and a water-soluble salt of a Group 2 metal.

7. A composition as claimed in any one of the preceding claims, wherein the fatty acid is stearic acid.

8. A composition as claimed in any one of

the preceding claims, wherein said sulphate is associated physically with 2—6% by weight of a Group 2 metal salt of the fatty acid.

5 9. A composition as claimed in any one of the preceding claims, which contains 20 to 60% by weight of said filler.

10 10. A composition as claimed in any one of the preceding claims, which includes a minor amount by weight of the polymer of an elastomer.

11. A composition as claimed in claim 10, which includes 5 to 20% by weight of the polymer of a synthetic rubber.

15 12. A composition comprising a blend of a polyolefin and a filler as claimed in any one of the preceding claims, wherein one or more known polyolefin additives is/are also present.

13. A composition as claimed in any one of the preceding claims, wherein the polymer is a Ziegler polyolefin.

14. A composition as claimed in claim 13, wherein said polyolefin is polyethylene.

25 15. A composition as claimed in any one of the preceding claims, wherein said sulphate is calcium sulphate.

16. A composition as claimed in any one of the preceding claims, which comprises as the polymer component thereof more than one polyolefin having a linear molecular structure.

30 17. A composition as claimed in claim 1 which comprises a Ziegler polyethylene substantially as hereinbefore described with reference to any of the Examples.

35 18. A process for preparing a polymer composition, which comprises blending a synthetic organic thermoplastic polymer with a finely-divided filler having an average particle size between 5 microns and 100 microns, said filler comprising a Group 2 metal sulphate having therewith in physical association (as specified herein) a higher fatty acid (as specified herein) or a salt or an ester thereof.

19. A process as claimed in claim 18, wherein said polymer is a polyolefin.

45 20. A process as claimed in claim 19, wherein a mixture comprising said polyolefin and said sulphate filler is blended by mechani-

cal working at an elevated temperature.

21. A process as claimed in claim 19 or claim 20, wherein the polyolefin is Ziegler 50 polyethylene or polypropylene.

22. A process as claimed in any one of claims 19 to 21, wherein a polyolefin or mixture of polyolefins is blended with between 20 and 100% (by weight of said polyolefin(s)) 55 of filler.

23. A process as claimed in any one of claims 18 to 22, wherein the filler has an average particle size between 5 and 65 microns.

24. A process as claimed in any one of claims 18 to 23, wherein said filler is a Group 2 metal sulphate in physical association with a Group 2 metal salt of a higher fatty acid. 60

25. A process as claimed in claim 24, wherein said fatty acid is stearic acid. 65

26. A process as claimed in claim 24 or claim 25, wherein said Group 2 metal is calcium.

27. A process for preparing a polyolefin composition, which comprises forming a blend of a Ziegler polyolefin (or a mixture thereof) and a finely-divided Group 2 metal sulphate having therewith in physical association (as specified herein) 2 to 6% by weight of a Group 2 metal salt of a higher fatty acid, said sulphate having an average particle size between 5 and 100 microns. 70 75

28. A process as claimed in claim 27, which comprises mixing Ziegler polyethylene with calcium sulphate in physical association with 3 to 5% by weight of calcium stearate, mixing being carried out at an elevated temperature to form a blend. 80

29. A polymer composition when prepared by the process claimed in any one of claims 18 to 28. 85

30. A shaped article formed wholly or partly from a polymer composition as claimed in any one of claims 1 to 17 and 29.

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